

SPECIFICATION AMENDMENTS

On page 1, insert above line 1, insert--Priority Claim

The present application claims priority on European Patent Application 03291660.3 filed 04 July 2003.--

On page 1, above line 1, insert--Field of the Invention--

Paragraph on line 1 of page 1 has been amended as follows:

--The present invention relates ~~is directed~~ to a process to prepare base oils or the intermediate waxy raffinate product in a high yield from a Fischer-Tropsch synthesis product.--

On page 1, above line 5, insert--Background of the Invention--

Paragraph on line 5 of page 1 has been amended as follows:

-- Such processes are known from WO-A-9941332, US-A-Pat. No.6080301, EP-A-0668342, US-A-Pat. No.6179994 or WO-A-02070629. These processes all comprise some kind of hydroisomerisation of the Fischer-Tropsch synthesis product followed by a dewaxing step of the higher boiling fraction obtained in said hydroisomerisation.--

Paragraph on line 11 of page 1 has been amended as follows:

-- WO-A-02070629, for example, describes a process wherein the C5 plus fraction of a Fischer-Tropsch synthesis product is first subjected to a hydrocracking/
~~hydroisomerising~~ hydroisomerizing step in the presence of a catalyst consisting of platinum on an amorphous silica-alumina carrier. The effluent of this conversion step is separated into middle distillate products and a base oil precursor fraction and a higher boiling fraction. The base oil precursor fraction is catalytically dewaxed in the presence of a platinum-ZSM-5 based catalyst and the heavy fraction is recycled to the hydrocracking/
~~hydroisomerising~~ hydroisomerizing step.--

On page 2, delete line 1-2.

On page 2, above line 3, insert--Summary of the Invention--

Paragraph on line 3 of page 2 has been amended as follows:

-- ~~The following process achieves this object. Process~~ The invention provides a process to prepare base oils from a Fischer-Tropsch synthesis product by

- (a) separating the Fischer-Tropsch synthesis product into a fraction (i) boiling in the middle distillate range and below, a heavy ends fraction (iii) and an intermediate base oil precursor fraction (ii) boiling between fraction (i) and fraction (iii),
- (b) subjecting the base oil precursor fraction (ii) to a catalytic hydroisomerisation and catalytic dewaxing process to yield one or more base oil grades,
- (c) subjecting the heavy ends fraction (iii) to a conversion step to yield a fraction (iv) boiling below the heavy ends fraction (iii) and
- (d) subjecting the high boiling fraction (v) of fraction (iv) to a catalytic hydroisomerisation and catalytic dewaxing process to yield one or more base oil grades.

On page 2, after line 20, insert --

Brief Description of the Drawings

The invention will also be illustrated by making use of Figures 1-4.

Figure 1 illustrates a state of the art process of WO-A-02070629.

Figure 2 illustrates a process according to the invention.

Figure 3 illustrates a process according to the invention.

Figure 4 illustrates a process according to the invention.

Figure 5 illustrates a process according to the invention.--

On page 2, above line 21, insert--Detailed Description of the Invention--

Paragraph on line 21 of page 2 has been amended as follows:

-- Applicants have found that by directly subjecting the fraction of the intermediate fraction (ii) of the Fischer-Tropsch synthesis product and the high boiling fraction (v) as obtained in step (c) to a selective isomerisation and dewaxing step a higher yield to base oils relative to the Fischer-Tropsch synthesis product may ~~can~~ be obtained.--

Paragraph on line 28 of page 2, ending on line 11 of page 3, has been amended as follows:

– Without intending to be bound by the following theory it is believed that the high yield to base oils is achieved in that the fraction boiling in the base oil range, i.e. fractions (ii) and (v), are directly contacted with the ~~he~~-catalytic isomerisation and dewaxing catalysts. In the prior art process of WO-A-02070629 the corresponding fraction of the Fischer-Tropsch synthesis product was first contacted with a catalyst which would convert a large part to middle distillate products and lower boiling products. By using this different line-up the conversion of potential base oil molecules in the Fischer-Tropsch synthesis product to middle distillate molecules is minimized. Furthermore in the process of WO-A-02070629 the heavy fraction as obtained in the hydrocracking/~~hydroisomerising~~ hydroisomerizing step is recycled to said step. This results in that more potential base oil molecules are converted to middle distillate molecules.–

Paragraph on line 12 of page 3 has been amended as follows:

– The Fischer-Tropsch synthesis product can be obtained by well-known processes, for example the so-called commercial Sasol process, the Shell Middle Distillate Process or by the non-commercial Exxon process. These and other processes are for example described in more detail in EP-A-776959, EP-A-668342, US-A-Pat.No.4943672, US-A-Pat.No.5059299, WO-A-9934917 and WO-A-9920720. Typically these Fischer-Tropsch synthesis products will comprise hydrocarbons having 1 to 100 and even more than 100 carbon atoms. The hydrocarbon product will comprise iso-paraffins, n-paraffins, oxygenated products and unsaturated products. The feed to step (a) or any fractions obtained in step (a) may be hydrogenated in order to remove any oxygenates or unsaturated products. The process of the present invention is especially advantageous when a substantial part, preferably more than 10 wt%, more preferably more than 30 wt% and even more preferably more than 50 wt% of the Fischer-Tropsch synthesis product boils above 550 °C. An example of a suitable process which may prepare such a heavy Fischer-Tropsch synthesis product is described in WO-A-9934917 and in AU-A-698392.–

Paragraph on line 1 of page 4 has been amended as follows:

– In step (a) the Fischer-Tropsch synthesis product is separated into a fraction (i) boiling in the middle distillate range and below, a heavy ends fraction (iii) preferably, having an initial boiling point between 500 and 600 °C and an intermediate base oil precursor fraction (ii) boiling between fraction (i) and fraction (iii). Suitably the Fischer-Tropsch synthesis

product is first fractionated at atmospheric pressure or higher to obtain fraction (i) boiling in the middle distillate range and below. Fractionation may be performed by flashing or distillation. The middle distillate range is sometimes defined as the fraction boiling predominately, i.e. for more than 90 wt%, between 200 and 350 °C and it comprises the gas oil and kerosene fractions, which can be isolated from the Fischer-Tropsch synthesis product. The residue or bottom product of the atmospheric fractionation is further separated at near vacuum pressure to the heavy ends fraction (iii) having an initial boiling point between 500 and 600 °C and the intermediate base oil precursor fraction (ii). More preferably the $T_{10wt\%}$ recovery point of the heavy ends fraction (iii) is between 500 and 600 °C.—

Paragraph on line 23 of page 4, ending on line 9 of page 5 has been amended as follows:

-- In step (b) the base oil precursor fraction (ii) is subjected to a catalytic hydroisomerisation and catalytic dewaxing process to yield one or more base oil grades. These catalytic processes are defined according to this invention as processes[[,]] which are selective for reducing the pour point of this fraction while minimising the conversion of molecules boiling above 370 °C to molecules boiling below 370 °C. It should be noted that when lower temperature pour points are desired for the base oil, more molecules will, even by the more selective isomerisation and dewaxing processes, be converted to fractions boiling below 370 °C. Selective isomerisation and dewaxing processes are preferably processes wherein less than 40 wt%, more preferably less than 30 wt%, of the feed to step (b) is converted to a fraction boiling below 370 °C when preparing a base oil having a kinematic viscosity at 100 °C of 5 cSt and having a pour point of -27 °C and a Noack volatility of 10 wt%. Examples of processes having the above described selectivity to base oils are well known and will be described below.—

Paragraph on line 13 of page 5 has been amended as follows:

-- Examples of possible isomerisation catalysts comprise one or more Group VIII metal, for example nickel, cobalt platinum or palladium on a refractory oxide carrier. Examples of specific catalysts are Pt on silica-alumina carrier (ASA), Pd on ASA, PtNi on ASA, PtCo on ASA, PtPd on ASA, CoMoCu on ASA, NiMoCu on ASA, NiW on ASA, NiWF on alumina, PtF on ASA, NiMoF on alumina. As a separate dewaxing step use may can be made in step (b) of the well known catalytic dewaxing processes wherein catalysts are used comprising medium pore size molecular sieves and a hydrogenation component, preferably a noble metal such as platinum or palladium. Examples of such processes are those based on

SAPO-11 as described in for example EP-A-458895, ZSM-5 as for example described in EP-B-832171, ZSM-23 as described in for example EP-A-540590 and EP-A-092376, ZSM-22 as for example described in US-A-Pat. No. 4574043, mordenite as for example described in US-A-Pat. No. 6179994 and ferrierite as for example described in EP-A-1029029.—

Paragraph on line 1 of page 6 has been amended as follows:

— If step (b) is carried out using a single catalyst process, catalyst may be used based on for example catalysts comprising platinum-zeolite-beta, as described in for example US-A-Pat.No. 5885438, or ZSM-23 or ZSM-22 based catalysts as for example described in EP-A-536325. Preferably use is made of a process which makes use of a ZSM-12 based catalyst as for example described in WO-A-0107538.—

Paragraph on line 9 of page 6 has been amended as follows:

— Advantageously an isomerisation step using a catalyst based on zeolite-beta is combined with a selective catalytic dewaxing step wherein use can be made of the dewaxing catalysts described above. Examples of the use of platinum-zeolite-beta catalysed step followed by a more selective dewaxing step using a platinum-ZSM-23 catalysed step is for example in US-A-Pat.No. A-4919788 and EP-A-1029029. The ZSM-23, ZSM-22 and ZSM-12 catalysts may also be used in a cascade dewaxing operation wherein the final dewaxing is performed making use of a more restricted pore size zeolite like for example ZSM-5, ZSM-11 or ferrierite as for example described in US-A-Pat.No. 4599162.—

Paragraph on line 16 of page 7 has been amended as follows:

— It has also been found possible to make more than one viscosity grade base oil with the process according to the invention. By obtaining a base oil precursor fraction (ii) in step (a) having a more broad boiling range more base oil grades may advantageously be obtained in step (e). Preferably the difference between the $T_{10wt\%}$ recovery point and the $90wt\%$ $T_{90wt\%}$ recovery point in the boiling curve is larger than 100 °C. In this mode the effluent of step (b) is separated into various distillate fractions comprising two or more base oil grades. In order to meet the desired viscosity grades and volatility requirements of the various base oil grades preferably off-spec fractions boiling between, above and/or below the desired base oil grades are also obtained as separate fractions. These fractions and any fractions boiling in the gas oil range or below may advantageously be recycled to step

(a). Alternatively fractions obtained boiling in the gas oil range or below may suitably be used as a separate blending component to prepare a gas oil fuel composition.--

Paragraph on line 1 of page 8 has been amended as follows:

-- The separation into the various fractions in step (e) may suitably be performed in a vacuum distillation column provided with side strippers to separate the fraction from said column. In this mode it is found possible to obtain for example a 2-3 cSt product, a 4-6 cSt product and a 7-10 cSt product simultaneously from a single base oil precursor fraction (ii). The ~~viscositie~~ viscosity values are the kinematic viscosity at 100 °C.--

Paragraph on line 11 of page 8 has been amended as follows:

-- In step (c) the heavy ends fraction (iii) is subjected to a conversion step to yield a fraction (iv) boiling below the heavy ends fraction (iii). Step (c) may be performed by any conversion process capable of converting the heavy Fischer-Tropsch wax to lower boiling hydrocarbon compounds. If the conversion product of step (c) is to contain a high content of olefinic compounds preferably a conversion process is applied which operates in the absence of added hydrogen. Examples of suitable processes which operate in the absence of added hydrogen are the well known thermal cracking process as for example described in US-A-Pat. No.6703535 and the catalytic cracking process as for example described in US-A-Pat. No.4684759. If on the other hand the conversion product of step (c) is to contain almost no olefins preferably a process is applied which is performed in the presence of added hydrogen. An example of a suitable process is the well known hydroisomerisation/hydrocracking process.--

Paragraph on line 29 of page 8, ending on line 20 of page 9 has been amended as follows:

-- Preferably a hydrocracking/ hydroisomerisation reaction takes place in step (c). Step (c) is preferably performed in the presence of hydrogen and a catalyst, which catalyst can be chosen from those known to one skilled in the art as being suitable for this reaction. Examples of such catalysts are the isomerisation catalysts as described above when discussing step (b). Catalysts for use in step (c) typically are amorphous catalysts comprising an acidic functionality and a hydrogenation/dehydrogenation functionality. Preferred acidic ~~functionality's~~ functionalities are refractory metal oxide carriers. Suitable

carrier materials include silica, alumina, silica-alumina, zirconia, titania and mixtures thereof. Preferred carrier materials for inclusion in the catalyst for use in the process of this invention are silica, alumina and silica-alumina. A particularly preferred catalyst comprises platinum, platinum or platinum and palladium supported on a silica-alumina carrier. If desired, the acidity of the catalyst carrier may be enhanced by applying a halogen moiety, in particular fluorine or chlorine, or a phosphorous moiety to the carrier. Examples of suitable hydrocracking/hydroisomerisation processes and suitable catalysts are described in WO-A-200014179, EP-A-532118 and the earlier referred to EP-A-776959.--

Paragraph on line 21 of page 9 has been amended as follows:

-- Preferred hydrogenation/dehydrogenation ~~functionality's~~ functionalities are Group VIII non-noble metals, for example nickel and more preferably Group VIII noble metals, for example palladium and most preferably platinum or platinum and palladium. The catalyst may comprise the hydrogenation/dehydrogenation active component in an amount of from 0.005 to 5 parts by weight, preferably from 0.02 to 2 parts by weight, per 100 parts by weight of carrier material. A particularly preferred catalyst for use in the hydroconversion stage comprises platinum in an amount in the range of from 0.05 to 2 parts by weight, more preferably from 0.1 to 1 parts by weight, per 100 parts by weight of carrier material. The catalyst may also comprise a binder to enhance the strength of the catalyst. The binder ~~can~~ may be non-acidic. Examples are alumina, silica, clays and other binders known to one skilled in the art.--

Paragraph on line 28 of page 12, ending on line 13 of page 13 has been amended as follows:

--The suitable thermal cracking step employed in step (c) is intended to crack the paraffin molecules into lower molecular weight olefins. The process may be performed in the liquid or vapor phase. Examples of liquid phase process configurations are the batch pyrolysis reactors such as employed in delayed coking or in cyclic batch operations. The process may also be carried out in the gas phase wherein a continuous flow-through operation is preferred. In such a process the feed is first preheated to a temperature sufficient to vaporize most or all of the feed after which the vapor is passed through a tube or tubes. A desirable option is to bleed any remaining nonvaporized hydrocarbons prior to entering the tubes in the cracking furnace. Preferably, the thermal cracking is conducted in the presence of steam, which serves as a heat source and also helps suppress coking in the

reactor. Details of a typical steam thermal cracking process may be found in US-A-Pat. No. 4042488.--

Paragraph on line 11 of page 14 has been amended as follows:

-- In the event step (c) is performed using a catalytic cracking process, of which the fluid catalytic cracking (FCC) process is an example, the following conditions are preferred. Preferably the feed will be contacted with a catalyst at a temperature between 450 and 650 °C. More preferably the temperature is above 475 °C. The temperature of preferably below 600 °C to avoid excessive overcracking to gaseous compounds. The process may be performed in various types of reactors. Because the coke make is relatively small as compared to a FCC process operating on a petroleum derived feed it is possible to conduct the process in a fixed bed reactor. In order to be able to regenerate the catalyst more ~~simple~~simply, preference is nevertheless given to either a fluidized bed reactor or a riser reactor. If the process is performed in a riser reactor the preferred contact time is between 1 and 10 seconds and more preferred between 2 and 7 seconds. The catalyst to oil ratio is preferably between 2 and 20 kg/kg. It has been found that good results may be obtained at low catalyst to oil ~~ratio's~~ ratios of below 15 and even below 10 kg/kg.--

Paragraph on line 32 of page 14, ending on line 14 of page 15 has been amended as follows:

--The catalyst system used in the catalytic cracking process in step (c) will at least comprise of a catalyst comprising of a matrix and a large pore molecular sieve. Examples of suitable large pore molecular sieves are of the faujasite (FAU) type as for example Zeolite Y, Ultra Stable Zeolite Y and Zeolite X. The matrix is preferably an acidic matrix. Examples of suitable catalysts are the commercially available FCC catalysts. The catalyst system of the process may advantageously also comprise of a medium pore size molecular sieve such as to also obtain a high yield of propylene next to the gasoline fraction. Preferred medium pore size molecular sieves are zeolite beta, Erionite, Ferrierite, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23 or ZSM-57. The weight fraction of medium pore crystals on the total of molecular sieves present in this process is preferably between 2 and 20 wt%.--

Paragraph on line 3 of page 17, ending on line 6 of page 18 has been amended as follows:

--The above referred to oligomerisation step (f) is intended to maximize the yield of base oils by oligomerizing the olefins present in the fraction boiling below 370 °C and especially boiling in the gasoline range as obtained in step (c). In a preferred embodiment the olefinic effluent of step (c) is provided to step (a) to obtain an olefinic fraction (i) which can be directly used in step (f) or may be further fractionated before being used in step (f). In such a scheme the feed to step (f) will also comprise the lower boiling compounds as present in the Fischer-Tropsch synthesis product. Because such a product may also contain olefins oligomerization of these olefins will then also take place in step (f). During oligomerization the lighter olefins are converted into heavier products. The molecules boiling in the base oil range as obtained in step (f) will have an excellent viscosity index making them suitable to be blended with the base oil products as obtained in steps (b) and (d). In the event the pour point is too high, the oligomerization product may be send sent to a catalytic dewaxing step. In a preferred embodiment this dewaxing can be performed by co-feeding this fraction with the feed of step (b) or alternatively of step (d) to their respective dewaxing processes. Even more preferred is to send the oligomerization product to step (a) in order to simplify the number of distillation steps before performing the dewaxing in step (b). In order to avoid a build up of paraffins boiling in the same boiling range as the olefins which are converted a bleed stream is preferably present. In a preferred embodiment step (f) is performed in a catalytic distillation in which simultaneously the olefins are converted to base oil molecules, which due to their higher boiling point are recovered at the bottom of the distillation column. Unreacted olefins may be are obtained at or near the top of the column and ~~can~~ may be recycled to the catalytic distillation column.--

Paragraph on line 7 of page 18 has been amended as follows:

--The oligomerization of olefins has been well reported in the literature, and a number of processes are available. See, for example, US-A-Pat. No. 6706936, US-A-Pat. No. 20040029984, US-A-Pat. No. 6703535, US-A-Pat. No. 4417088, US-A-Pat. No. 4434308, US-A-Pat. No. 4827064, US-A-Pat. No. 4827073 and US-A-Pat. No. 4990709. Various types of reactor configurations may be employed, with the fixed catalyst bed reactor being used commercially. More recently, performing the oligomerization in an ionic liquids media has been proposed, since the contact between the catalyst and the reactants is efficient and the separation of the catalyst from the oligomerization products is facilitated. But ~~also~~ the catalytic distillation process may also be used advantageously.--

Paragraph on line 21 of page 18 , ending on line 9 of page 19 has been amended as follows:

-- Preferably, the oligomerized product will have an average molecular weight at least 10 percent higher than the initial feedstock, more preferably at least 20 percent higher. The oligomerization reaction will proceed over a wide range of conditions. Typical temperatures for carrying out the reaction are between 0 °C and 430 °C. Other conditions include a space velocity from 0.1 to 3 LHSV and a pressure from 0 to 2000 psig. Catalysts for the oligomerization reaction can be virtually any acidic material, such as, for example, zeolites, clays, resins, BF₃ complexes, HF, H₂SO₄, AlCl₃, ionic liquids (preferably ionic liquids containing a Bronsted or Lewis acidic component or a combination of Bronsted and Lewis acid components), transition metal-based catalysts (such as Cr/SiO₂), superacids, and the like. In addition, non-acidic oligomerization catalysts including certain organometallic or transition metal oligomerization catalysts may be used, such as, for example, zirconocenes. For illustration purposes reference is made to US-A-Pat. No. 6703535 which publication illustrates the preparation of a base oil from a an olefinic Fischer-Tropsch derived feed by means of oligomerisation.--

Paragraph on line 8 of page 20 has been amended as follows:

-- The waxy raffinate may be sold as a separate product. For example it may be prepared at a gas producing location and further processed to end products like for example base oils at a location ~~more-closer~~ to the end consumers. The raffinate itself may find use as feedstock to prepare base oils as described above. The waxy raffinate product ~~may can~~ also advantageously be used as steam cracker feedstock to prepare lower olefins, for example ethylene and propylene. Because of its high paraffin content, high yields to lower olefins are possible when using such a feedstock as steam cracker feedstock.--

On page 20, delete line 29-32.

On page 21, delete line 1-8.

Paragraph on line 12 of page 22 has been amended as follows:

-- Figure 3 is a process as in Figure 2 wherein the products obtained in the hydrocracking/hydroisomerisation step 44 are is recycled to the first separation unit 42. As

can be seen by comparing Figure 2 with Figure 3 a considerable reduction in unit operations is achieved. In a Fischer-Tropsch synthesis process step 40 a Fischer-Tropsch product 41 is prepared. This product 41 is separated by means of distillation 42 in one or more middle distillate fractions 46, 47, which may be naphtha, kerosene and gas oil, into a base oil precursor fraction 48 and a higher boiling fraction 43. Distillation 42 may be a atmospheric distillation and a vacuum distillation scheme as in Figure 1. The higher boiling fraction 43 is fed to a hydrocracking/hydroisomerisation step 44 yielding a cracked product 45, which is recycled to distillation 42.--

Paragraph on line 11 of page 23 has been amended as follows:

-- Figure 4 illustrates a process to prepare a waxy raffinate product 65. Figure 4 shows a Fischer-Tropsch synthesis process step 60 a Fischer-Tropsch product 61 is prepared. This product 61 is separated by means of distillation 62 in one or more middle distillate fractions 63, 64, which may be naphtha, kerosene and gas oil, into a waxy Raffinate product 65 and a higher boiling fraction 66. Distillation 62 may be an atmospheric distillation and a vacuum distillation scheme as in Figure 1. The higher boiling fraction 66 is fed to a heavy ends conversion step 67 yielding a product 68 containing on average lower boiling molecules than the feed 66. The heavy ends conversion step 67 may be any of the steps described above for step (c). The product 68 is recycled to distillation 62. Optionally the waxy Raffinate 65 may be used as feed for of a steam cracker furnace dedicated for such a feed. In a possible embodiment also a naphtha fraction 63 is fed to a dedicated steam cracker furnace. The gas oil product 64 may be advantageously sold as a separate product. Because of its high Cetane Number it may be use-used, more advantageously as an automotive gas oil fuel component than as a steam cracker feed stock.--

Paragraph on line 1 of page 24 has been amended as follows:

-- Figure 5 is as Figure 3 except that for step (c) a fluid catalytic cracking process (70) is performed. Fraction (64) is now rich in olefins and therefore also gasoline fraction (63) which is used as feed to a catalytic oligomerisation-distillation column (71) is rich in olefins. The bottom stream (72) rich in compounds boiling in the base oil range is ~~send~~ sent to dewaxing step (49) to remove possible waxy compounds formed in column (71). The light compounds (74) are recycled to oligomerisation step (71) and a bleed stream (73) is present to

avoid a build up of paraffins. Gas oil (47) may find application as ethylene ~~crack~~cracker feedstock, industrial gas oil or as automotive gas oil.--

Paragraph on line 13 of page 27 has been amended as follows:

--Base oil yield as the fraction boiling between 400 and 540 °C of the dewaxed oil, having a kinematic viscosity at 100 °C of 5 cSt and a pour point of -20 °C starting from an waxy Raffinate feed (ii) is 70 wt%. This yield is achievable when the base oils are obtained by subjecting the fraction (ii) to a catalytic dewaxing process using a silica bound platinum ZSM-12 type of catalyst as described in US-A-Pat. No. 6576120. --

On page 29 above line 1, insert --We claim:--